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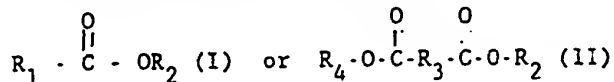
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(54) Hydrogenation of esters into alcohols

(57) A process for hydrogenation of esters of the formulae



wherein R_1 represents hydrogen or a hydrocarbyl group, wherein R_2 and R_3 represent a hydrocarbyl group, and wherein R_4 represents a hydrocarbylene group, in the presence of hydrogen and carbonmonoxide and a catalyst system, obtainable by combining the following components:

- (a) a compound containing a cation of an element of group VIII of the Periodic Table of the Elements,
- (b) an alcoholate of an alkali metal and/or alkaline earth metal,
- and
- (c) an alcohol.

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PROCESS FOR HYDROGENATION OF ESTERS
INTO ALCOHOLS

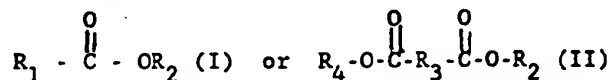
The invention relates to a process for the hydrogenation of esters and more particularly to a process for the hydrogenation of esters into alcohols with a hydrogen containing gas and in the presence of a catalyst system.

5 Such processes are in general known from a great variety of literature and are using a large number of diverging types of catalysts. However, these conventional industrial scale catalytic hydrogenation processes have the disadvantage that they are using rather pure hydrogen at high pressures such as disclosed in e.g.
10 U.S. patents Nos. 4,628,130 and 4,346,240 and German patent No. 1,768,262 and/or high temperatures or that they are using catalyst systems, which can only be removed from the desired product by laborious methods, which inevitably cause significant additional
15 costs.

 It will be appreciated that there is still a growing need for an economically attractive process for hydrogenation of esters into alcohols, which should not inevitably require the use of rather pure hydrogen gas, but should be carried out in the presence of
20 cheaper hydrogen containing gas such as synthesis gas or other commercially available hydrogen containing gas mixtures, and should use simpler and therefore cheaper catalyst systems.

 Therefore, it is an object of the present invention to provide such an improved process.

25 As result of extensive research and experimentation an improved process was surprisingly found for the hydrogenation of esters of the formulae



wherein R_1 represents hydrogen or a hydrocarbyl group, R_2 and R_4 represent a hydrocarbyl group, and wherein R_3 represents a hydrocarbylene group, in the presence of hydrogen and carbonmonoxide and a catalyst system, obtainable by combining the following components:

- (a) a compound containing a cation of an element of group VIII of the Periodic Table of the Elements,
- (b) an alcoholate of an alkali metal and/or alkaline earth metal, and
- (c) an alcohol.

Preferably esters are hydrogenated, wherein R_1 represents an alkyl or alkenyl group containing 1-20 carbonatoms and more preferably 3-12 carbon atoms, an aryl group or aralkyl group, containing 1-6 carbon atoms in the alkyl residue, the aryl being more preferably phenyl and the aralkyl being benzyl, wherein R_2 and R_4 are hydrocarbyl groups as specified hereinbefore for R_1 and are the same or different in one molecule, and wherein R_3 represents an alkylene group or an alkenylene group of 1-10 carbon atoms or an arylene group, and more preferably phenylene or naphthylene.

As component (a) several salts of elements of group VIII of the Periodic Table of the Elements may be used and preferably salts of palladium, cobalt or nickel. Most preferred are nickel salts. The anion of the salt in component (a) may be derived from a great variety of acids and preferably from carboxylic acids or hydrochloric acid, sulphuric acid nitric acid phosphoric acid, or sulphonic acids.

Among these acids preference is given to alkanoic acids having 1-10 carbon atoms in the chain such as formic acid, acetic acid, propionic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid, 3-methylbutanoic acid, 2,2-dimethylpropanoic acid, hexanoic acid, heptanoic acid and octanoic acid, oxalic acid or to paratoluene sulphonic acid. More preference is given to formic acid, acetic acid and oxalic acid.

Most preferably nickel formate, nickel acetate, nickel oxalate or nickel tosylate are used.

However, the anions of the component (a) also may be derived from dicarboxylic acids such as malonic acid, dimethyl malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, phthalic acid, isophthalic acid and terephthalic acid.

The carboxylic acids from which the anion of component (a) may be derived may contain substituents, for example alkoxy groups, particularly those having not more than five carbon atoms, hydroxy groups, cyano groups and fluorine, chlorine, bromine and iodine atoms.

Examples of such carboxylic acids are glycolic acid, 2-hydroxypropionic acid, 3-hydroxypropionic acid, glyceric acid, tartronic acid, malic acid, tartaric acid, tropic acid, benzilic acid, salicylic acid, anisic acid, gallic acid, 3,5-dichlorobenzoic acid, 3,5-dibromobenzoic acid, cyano acetic acid, monofluoro acetic acid, difluoroacetic acid, trifluoroacetic acid and trichloroacetic acid.

A mixture of the salts may also be used in component (a) e.g. of a formate and an oxalate of a formate and an acetate, or of an acetate and an oxalate.

The salts to be used as component (a) may contain crystal water, but are preferably free therefrom.

The alcoholate to be used as component (b) is preferably a sodium alcoholate or a potassium alcoholate. Among the alcoholates preference is given to alkoxides, particularly to those having from 1 to 20 carbon atoms per molecule, such as sodium methoxide, sodium ethoxide, sodium propoxide, sodium butoxide, sodium isobutoxide, sodium tert-pentoxide and potassium 2-methyldodec-2-oxide.

Component (b) may also consist of a mixture of alcoholates, e.g. potassium tert.butoxide and potassium tert.pentoxide or sodium tert.butoxide and sodium tert.pentoxide.

The alcohol of component (c) may be cycloaliphatic or aliphatic, but is preferably aliphatic. Preference is given to alkanols, in particular to those having in the range of from 1 to 20 carbon atoms per molecule. Among the latter alkanols those

having in the range of from 4 to 20 carbon atoms per molecule are preferred. Tertiary alcohols are more preferred. Examples of suitable alkanols are tert.butyl alcohol, tert.pentyl alcohol, hexanol, heptanol and alkanols with from 8 to 20 carbon atoms per molecule. Tert.butyl alcohol and tert.pentyl alcohol are particularly preferred.

Polyhydric alcohols may also be used, for example ethylene glycol, propylene glycol, 1,3-dihydroxypropanen, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2-pentanediol or glycerol.

Component (b) may be a mixture of alcohols, for example of tert.butyl alcohol and ethylene glycol or of tert.phenyl alcohol and 1,4-butanediol.

The process of the present invention is preferably used for hydrogenation of esters according to formula I wherein R_1 represents aryl and more preferably phenyl or naphthyl and wherein R_2 represents an alkyl residue or aralkylresidue and preferably methyl, ethyl or benzyl, wherein R_3 represents phenylene, naphthylené or alkylene or alkenylene having 1-4 carbon atoms, and wherein R_4 represents an alkyl residue or aralkyl residue. More particularly the hydrogenation process of the present invention is used for the conversion of alkanolic acid esters or, aromatic esters such as lower alkyl propionate, lower alkyl benzoate, lower alkyl phenylacetate, lower alkyl naphtoate, di(lower alkyl)terephthalate, di(lower alkyl)phthalate, di(lower alkyl)isophthalate.

More preferably methyl propionate, methyl undecenoate, methyl benzoate, ethylbenzoate, di(methyl)phthalate, di(methyl)isophthalate, di(methyl)terephthalate, di(ethyl)phthalate, di(ethyl)isophthalate or di(ethyl)terephthalate are hydrogenated according to the present process.

The activation of the catalyst system, providing the most attractive results, may be reached by keeping the mixed components under an atmosphere of nitrogen or any other suitable inert gas during 0.3 to 1 hour at a temperature in the range of from 20-60 °C and more preferably 35-50 °C.

The process according to the present invention may be carried out at a temperature and a pressure which are not critical and may vary within wide ranges. Preferably, a temperature in the range of from 30 °C to 150 °C and a pressure in the range of from 5 to 100 bar are used.

The process according to the present invention may be carried out with an organic diluent in which the catalytic system is dissolved or suspended. Suitably, a weight ratio of organic diluent to component (a) in the range of from 0.1 to 5000 is used, but this weight ratio may be lower than 0.1 or higher than 5000.

Any inert diluent may in principle be used. Examples of suitable diluents are ethers such as anisole, 2,5,8-trioxanonane (also referred to as "diglyme"), diethyl ether, diphenyl ether, diisopropyl ether and tetrahydrofuran; aromatic hydrocarbons, such as benzene, toluene, the three xylenes and ethylbenzene; halogenated aromatic compounds, such as chlorobenzene and o-dichlorobenzene; halogenated alkanes, such as dichloromethane and carbontetrachloride; alkanes, such as hexane, heptane, octane, 2,2,3-trimethylpentane and kerosene fractions; cycloalkanes, such as cyclohexane and methylcyclohexane; sulphones, such as diisopropyl sulphone, tetrahydrothiophene 1,1-dioxide (also referred to as "sulfolane"), 2-methyl-4-butylsulfolane and 3-methylsulfolane. Mixtures of two or more solvents may be used. Very good results have been obtained with ethers and the use of diglyme is most preferred.

The process according to the present invention is preferably carried out using a molar ratio of the starting ester to component (a) in the range of from 0.5:1 to 100:1 and, more preferably, from 1:1 to 50:1, but the use of molar ratios below 0.5 and above 100 is not excluded. The process may be carried out using a molar ratio of component (a) to component (b) which is not critical and may vary within wide ranges, preferably in the range of from 10:1 to 1:100.

The carbon monoxide and hydrogen may be used as pure gases or diluted with an inert gas such as an inert gas or nitrogen. The process according to the present invention may be suitably carried

out using a molar ratio carbon monoxide to hydrogen in the gaseous mixture suitably in the range of from 0.05 to 0.3. The carbon monoxide and hydrogen may be obtained by partial oxidation or steam reforming of hydrocarbons, for example of natural gas.

5 It is true, that catalyst systems containing the presently proposed components are known from e.g. U.S. patent No. 4,614,749 and Japanese patent application No. 56.169.634.

10 However, on the one hand in U.S. patent No. 4,614,749 such catalyst systems are only used for the preparation of methanol from syngas, whereas as additional components an alkali metal hydride and a carbonyl complex of one of the group VI metals are used. On the other hand the Japanese patent application No. 56.169.634 also discloses a process for the preparation of methanol from syngas mixtures using a catalyst, comprising a nickel compound being not
15 derived from the before-mentioned carboxylic acids, and an alkali metal alkoxide while moreover according to the examples 10-12 also alkali metal hydrides were included in these catalysts.

20 It will therefore be appreciated that a person skilled in the art could not find any teaching in these publications to come to the present process and that the attractive results obtained according to the process of the present invention using mixtures of hydrogen and carbon monoxide can only be regarded as surprising by such skilled person.

25 According to a specific embodiment of the process of the present invention methylpropionate, methyl benzoate, or methyl undecenoate is hydrogenated into methanol, and propanol; methanol and benzylalcohol and methanol and 1-undecenol respectively, at 80-120 °C and a total pressure of 30-50 bar, during a total reaction period of from 3-5 hours, showing attractive conversions.

30 The following examples further illustrate the invention without however restricting the scope thereof to these particular embodiments. All experiments were carried out in a 300 ml magnetically stirred Hastelloy C (Registered Trade Mark) autoclave. The reaction mixtures obtained were analyzed by means of gas-liquid
35 chromatography.

EXAMPLE 1

The autoclave is initially charged with 50 ml diglyme, 10 mmol nickel(II)formate and 20 mmol tert.amylalcohol.

The catalyst system was activated during 0.5 hour at 45 °C under nitrogen.

5 Thereafter 50 ml tert.amylalcohol, 60 mmol potassium tert.butylate and 20 ml methyl propionate were added. Carbon monoxide is added to a partial pressure of 5 bar, where hydrogen is added to a partial pressure of 30 bar at ambient temperature.

10 The reaction mixture was then heated up to 80 °C and kept at this temperature during 5 hours, whereas after 15 min hydrogen was added until a pressure increase of 35 bar and after 45 min carbon monoxide was added until a pressure increase of 5 bar and hydrogen was added until a partial pressure increase of 10 bar.

15 After termination of the reaction, the mixture was allowed to cool to room temperature and analyzed.

3.3 g methanol and 2.6 g propanol were found.

EXAMPLE 2

The autoclave is initially charged with 50 ml diglyme, 10 mmol nickel(II)formate and 20 mmol tert.amylalcohol.

20 The catalyst system was kept during 0.5 hour at 45 °C under nitrogen.

25 Thereafter 10 ml tert.amylalcohol in 40 ml diglyme, 60 mmol potassium tert.butylate and 10 ml methylpropionate were added. Carbon monoxide is added to a partial pressure of 5 bar while hydrogen is added to a partial pressure of 30 bar, whereafter the temperature was increased from 45 °C to 100 °C. The reaction mixture was kept at a temperature of 100 °C during 5 hours. After 10 min hydrogen was added until a pressure increase of 30 bar was reached.

30 After termination of the reaction the mixture was allowed to cool to room temperature and analyzed. 2.5 g methanol and 2.5 g propanol were found.

EXAMPLE 3

In about the same way as described under Example 2, an experiment was carried out, with the difference that the autoclave was kept at 120 °C for 3 hours, giving 3.2 g methanol and 3.5 g propanol.

5 EXAMPLE 4

In the same way as described under Example 2, an experiment was carried out, with the difference that carbon monoxide was added to a partial pressure of 2 bar instead of 5 bar, whereas the autoclave was kept at 120 °C for 5 hours, giving a yield of 2.0 g methanol and 3.1 g propanol.

10 EXAMPLE 5

In the same way as described under Example 2, an experiment was carried out with the difference that 10 ml methylbenzoate was included in the autoclave instead of 10 ml methyl propionate. The partial hydrogen pressure was 30 bar, while the autoclave was kept at 120 °C for 5 hours, giving a yield of 2.5 g methanol and 7.5 g benzylalcohol.

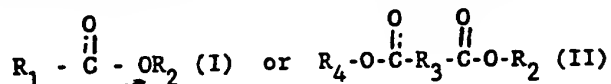
EXAMPLE 6

20 In about the same way as described under Example 2, an experiment was carried out with difference that 10 ml methylundecenoate was included in the autoclave instead of 10 ml methylpropionate, while after 5 min hydrogen was added until a pressure increase of 30 bar was reached. The autoclave was kept at 80 °C for 5 hours giving a yield of 2.4 g methanol and about 1 g 1-undecenol.

25

C L A I M S

1. A process for the hydrogenation of esters into alcohols, with comprises converting esters of the formulae



5 wherein R_1 represents hydrogen or a hydrocarbyl group, R_2 and R_4 represent a hydrocarbyl group, and wherein R_3 represents a hydrocarbylene group,

in the presence of hydrogen and carbonmonoxide and a catalyst system, obtainable by combining the following components:

- 10 (a) a compound containing a cation of an element of group VIII of the Periodic Table of the Elements,
(b) an alcoholate of an alkali metal and/or alkaline earth metal, and
(c) an alcohol.

15 2. A process as claimed in claim 1, characterized in that esters are hydrogenated, wherein R_1 represents an alkyl or alkenyl group containing 1-20 carbon atoms, an aryl group or aralkyl group, containing 1-6 carbon atoms in the alkyl residue, wherein R_2 and R_4 are hydrocarbyl groups as specified hereinbefore for R_1 and are the
20 same or different in one molecule, and wherein R_3 represents an alkylene group or an alkenylene group of 1-10 carbon atoms or an arylene group.

3. A process as claimed in any one of the claims 1 to 2, characterized in that R_1 represents an alkyl or alkenyl group
25 containing 3-12 carbon atoms, a phenyl group or benzyl group, and that R_3 represents a phenylene group.

4. A process as claimed in any one of the claims 1 to 3, characterized in that component (a) is a palladium, cobalt or nickel salt.

5. A process as claimed in any one of the claims 1 to 4, characterized in that a nickel salt is used.

6. A process as claimed in claim 5, characterized in that nickel formate, nickel acetate, nickel oxalate or nickel tosylate is used.

5 7. A process as claimed in any one of the claims 1 to 6, characterized in that component (b) consists of a sodium alcoholate or potassium alcoholate.

8. A process as claimed in claim 7, characterized in that sodium methoxide, sodium ethoxide, sodium propoxide, sodium butoxide,
10 sodium isobutoxide, sodium tert.pentoxide or potassium 2-methyldodec-2-oxide is used.

9. A process as claimed in any one of the claims 1 to 8, characterized in that as component (c) an alkanol having 4 to 20 carbon atoms is used.

15 10. A process as claimed in any one of the claims 1 to 9, characterized in that tert.butyl alcohol or tert.pentyl alcohol is used.

11. A process as claimed in any one of the claims 1 to 10, characterized in that the reaction is carried out at a temperature
20 in the range from 30 °C to 150 °C.

12. A process as claimed in any one of the claims 1 to 11, characterized in that the reaction is carried out at a pressure in the range of from 5 to 100 bar.

13. A process as claimed in any one of the claims 1 to 12, characterized in that the reaction is carried out in an organic
25 diluent.

14. A process as claimed in any one of the claims 1 to 13, characterized in that the weight ratio of organic diluent to component (a) is in the range of from 0.1 to 5000.

30 15. A process as claimed in any one of the claims 1 to 14, characterized in that the molar ratio of the starting ester to component (a) is in the range of from 0.5:1 to 100:1.

16. A process as claimed in claim 15, characterized in that the molar ratio is in the range of from 1:1 to 50:1.

17. A process as claimed in any one of the claims 1 to 16,
characterized in that molar ratio of the component (a) to component
(b) is in the range of from 0.1:1 to 100:1 is used.
18. A process as claimed in any one of the claims 1 to 17,
5 characterized in that an ether is used as diluent.
19. A process as claimed in claim 18, characterized in that
diglyme is used as diluent.
20. A process as claimed in any one of the claims 1 to 19,
characterized in that a molar ratio of carbon monoxide to hydrogen
10 in the range of from 0.05 to 0.3 is used.
21. A process as claimed in any one of the claims 1 to 20,
characterized in that methylpropionate, methyl benzoate, or methyl
undecenoate is hydrogenated.
22. A process for the hydrogenation of esters into alcohols
15 ~~restricting in~~ ^{according to} claim 1, substantially as described hereinbefore
with reference to the examples.
23. Alcohols obtained by the process for the hydrogenation of
esters according to claims 1 to 22.